Supporting Information for:

Crystal Structure of $Li_2B_{12}H_{12}$: a Possible Intermediate Species in the Decomposition of $LiBH_4$

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The XRD data were collected at room temperature with a Rigaku Ultra III* sealed tube (1.6 kW, Cu Kα) diffractometer. The TOPAS-Academic* program was used to index the pattern and to solve and refine the structure. The crystal structure was solved by the direct space searching method (simulated annealing). An ideal dodecahedron rigid body was defined for the $B_{12}H_{12}^{2-}$ anion, and dynamic occupancy correction was enabled during the annealing process. After decent agreement was achieved between observed and calculated patterns, the structure model was trimmed out by removing duplicated atoms in the rigid-body definition due to the incorporation of molecular and crystallographic symmetry operations and taking into account the special position requirement. The Rietveld refinement was still done with a rigid-body model since the powder pattern did not contain enough information to localize the individual atomic positions, especially due to the insensitivity of x-rays for H atoms. Though the B and H atoms were constrained, the B-B and B-H distances were allowed to vary. All displacement parameters were treated isotropically, and all like atoms were constrained to the same values.

First-principles calculations were performed within the plane-wave implementation of the generalized gradient approximation to density functional theory (DFT) using the PWscf package* (Baroni, S.; Dal Corso, A.; de Gironcoli, S.; Giannozzi, P. http://www.pwscf.org). We used a Vanderbilt-type ultrasoft potential with Perdew-Burke-Ernzerhof exchange correlation. A cutoff energy of 400 eV and a 4×4×4 k-point mesh were found to be enough for the total energy to converge within 0.5 meV/atom and 5 meV/Å.

The neutron vibrational spectrum for $Li_2B_{12}H_{12}$ at 4 K was measured at the National Institute of Standards and Technology Center for Neutron Research with the BT-4 Filter Analyzer Neutron Spectrometer using horizontal 20' collimations before and after the Cu(220) monochromator.

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*Certain commercial suppliers are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the NIST nor does it imply that the materials, equipment, or software identified are necessarily the best available for the purpose.

Table S1. Experimental and crystallographic details.

Crystal data	
Chemical formula	$Li_2B_{12}H_{12}$
M_r	155.70
Cell setting, space group	Cubic, $Pa\bar{3}$
Data collection temperature	Ambient
a, b, c (Å)	9.5771(2), 9.5771(2), 9.5771(2)
α, β, γ (°)	90, 90, 90
Volume (Å^3)	878.43(6)
Z	4
D_x (Mg m^{-3})	1.17747(8)
Radiation type	Cu Kα
Specimen color	White
Refinement	
Refinement method	Rietveld
R factors and goodness-of-fit	$R_p = 0.038$, $R_{wp} = 0.050$, $R_{exp} = 0.032$, $R_B = 0.008$, $S = 1.563$
Number of parameters	38
H-atom treatment	Rigid body (dodecahedron)
Weighting scheme	$1/\sigma^2$
$(\Delta/\sigma)_{max}$	<0.001
Result	
Li-H distances (Å)	2.077(7), 2.216(7)
B-H distance (Å)	1.205(13)
B-B distances (Å)	1.7800(32), 1.7984(14), 1.8002(16), 1.8034(24), 1.8102(32)
Li thermal parameter	4.7(2)
B, H thermal parameter	1.98(7)